Chemical conversion of various celluloses as treated in supercritical methanol

Y. Ishikawa, S. Saka?
Graduate School of Energy Science, Kyoto University, Sakyo-ku, Kyoto 606-8501, Japan
Tel/Fax: +81-75-753-4738; Shiro Saka, E-mail: saka@energy.kyoto-u.ac.jp

The chemical conversion of various celluloses as treated in supercritical methanol was studied with a batch-type reaction vessel. The supercritical methanol treatment at 350 ºC and 43 MPa was sufficient to convert various celluloses to the methanol-soluble without any catalyst. The decomposition rate was affected greatly by the form of cellulose rather than its crystallinity, and the rapid increase of the decomposition rate constant was observed in the vicinity of 270 ºC. The main products from cellulose decomposition were methyl ?- and ?-D-glucosides, levoglucosan, methylated oligomers and 5-hydroxymethylfurfural. Monomeric compounds such as methyl ?- and ?-D-glucosides were stable in supercritical methanol. Therefore, the high yield of the monomeric compounds could be obtained by the supercritical methanol treatment. These findings suggest that the supercritical methanol treatment of various cellulosic materials such as waste paper has a potential to obtain useful chemicals and liquid fuels without using fossil resources.

Introduction

Cellulose is renewable, carbon neutral and most abundant biomass resources in the world. However, cellulose is difficult to hydrolyze due to the crystalline structure, compared with starch. Therefore, these abundant cellulose resources such as waste papers have not been utilized efficiently, to date. Recently, supercritical water treatment has been considered to be an attractive alternative in science and technology for hydrolyzing cellulose, compared with enzymatic saccharification and acidic hydrolysis conversion methods. Some researchers reported that the supercritical treatment of water could convert cellulose rapidly to glucose [1,2]. However, the yields of glucose were generally low because glucose was also decomposed rapidly in supercritical water due to its critical temperature (T_C=374 ºC) being high. Therefore, it may be difficult to obtain the high yield of glucose steadily by the supercritical water treatment. In this study, therefore, methanol was selected as the solvent for supercritical treatment of cellulose, in which the critical temperature of methanol (T_C) to be 239 ºC and its critical pressure (P_C) to be 8.09 MPa would be much milder than that of water. Therefore, a supercritical methanol treatment of cellulose was evaluated to convert it into the liquids for useful chemicals or fuels.

Material and Methods

As cellulosic samples, microcrystalline cellulose (avicel), cotton linter and dissolving pulp were selected for the supercritical treatment of methanol. Methanol was fully fed to the 5 ml reaction vessel with 150 mg of cellulosic samples, and then it was attached to the batch-type supercritical methanol biomass conversion system. To start supercritical treatment of the sample, the reaction vessel was quickly heated by immersing it into the tin bath preheated at various temperatures and maintained at designated temperature and pressure with swaying left and right. To stop the reaction, the reaction vessel was moved into the water bath to quench. The reaction mixture obtained after the treatment was filtrated with 0.2μm membrane filter to separate methanol-insoluble and methanol-soluble portions. The methanol-insoluble portion was then dried and weighed to obtain its yield. The methanol-soluble portion was analyzed by using the liquid chromatography–mass spectrometry (LC-MS) and the high performance liquid chromatography (HPLC).

Results and Discussion

The supercritical methanol treatment at 350 ºC and 43 MPa for 7 min was sufficient to convert avicel which is in

a powder form to methanol-soluble portion completely. However, it required about 20 min for cotton linter and dissolving pulp which were in fiber form. This result suggested that cellulose decomposition in supercritical methanol is affected more greatly by the form of cellulose rather than the degree of its crystallinity.

Figure 1. shows the arrhenius plot for the decomposition rate constant of avicel in subcritical and supercritical methanol with those of methyl ?- and ?-D-glucosides. The decomposition rate constant of avicel increased rapidly at a temperature about 270 ℃, but not near T_C of methanol. However, for corn starch which is in helical structure and more amorphous nature with much less hydrogen bonds, a rapid change of the decomposition rate constants was not observed between 255 and 300 ℃. This result might suggest that some changes in crystalline microfibrils of cellulose, which became to be easy to decompose the microfibrils, occur in supercritical methanol above 270 ℃ and 26 MPa.

The main products from cellulose decomposition were, methyl ?- and ?-D-glucosides, levoglucosan, methylated oligomers and 5-hydroxymethylfurfural (5-HMF). Figure 2. shows the changes in the yields of the products from avicel as treated in supercritical methanol at 350 ℃ and 43 MPa. The total yield of the monomeric compounds was maximal at 3 min treatment and reached up to 34.8 wt%, which is 51.7 wt % of the cellulose liquefied in methanol. The reason why the high yield of monomeric compounds was obtained steadily by the supercritical methanol treatment of cellulose, compared with the supercritical water treatment, was that the decomposition rate constants of the monomeric compounds such as methyl ?- and ?-D-glucosides were considerably lower than that of avicel in supercritical methanol, as shown in Figure 1. [3]. The maximal yields of the monomeric compounds obtained from cotton linter and dissolving pulp was 11.0 and 21.4 wt%, respectively. This result indicated that the speedy liquefaction of cellulose is one of the most important factors to achieve the high yield of monomeric compounds. These findings suggest that the supercritical methanol treatment of various cellulosic materials has a potential to obtain useful chemicals and liquid fuels without using fossil resources.

References

[1] Saka S, Ueno T. Cellulose, 6, 1999, p.177.

[2] Sasaki M, Fang Z, Fukushima Y, Adschiri T, Arai K. Ind. Eng. Chem. Res, 39, 2000, p.2883.

[3] Ishikawa Y, Saka S. Cellulose (submitted).

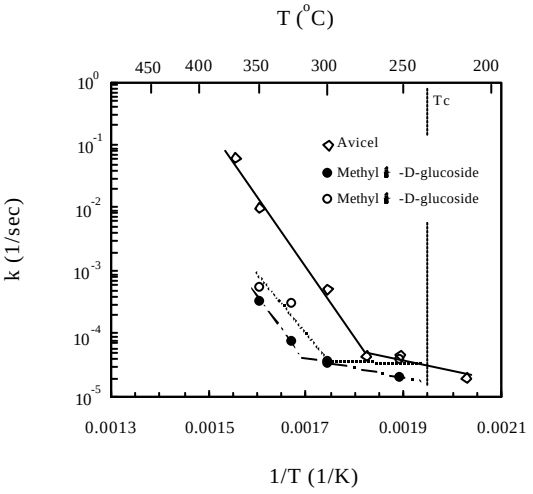

Figure 1. Arrhenius plot for the decomposition rate constants of avicel and methyl ?- and ?-D-glucosides in sub- and supercritical methanol.

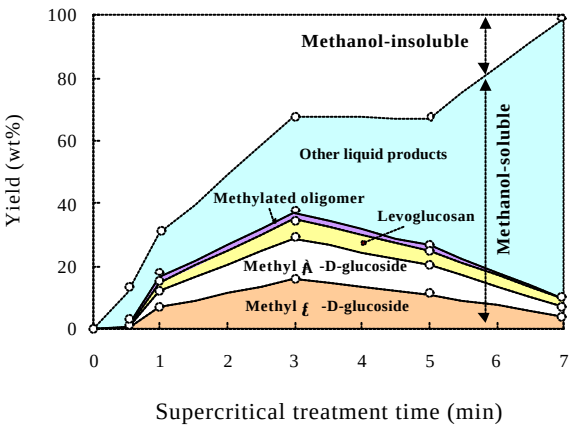

Figure 2. Changes in the yields of the products from avicel as treated in supercritical methanol at 350 °C and 43 MPa.